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The role of various hydrocarbon compounds in producing chemically-induced animal cancers has been well established by an impressive backlog of reported studies (Hartwell, 1957, Haddow, 1958). Many investigators have shown benzo-(a)pyrene to be one of the more active carcinogens. A recent publication by Sawicki, et al.,[1] reporting the extent of benzo(a)pyrene (also called 3,4-benzopyrene) associated with particulate matter collected from the air of several major cities, emphasizes the importance of knowing more about the occurrence of this and other related polynuclear hydrocarbons having demonstrated or presumed carcinogenic significance.

Such polynuclears are formed as combustion by-products during the burning of conventional fuels (coal, oil and gasoline) and cellulose materials such as wood, paper, and tobacco. Potential sources releasing these materials to the atmosphere include domestic and industrial heating processes, automobile engine exhausts, incinerators burning wood, paper, cardboard and other organic material contained in municipal and industrial wastes, and certain specialized industrial processes such as coke, carbon black and petrochemical production, and industries producing or processing coal tars.

The extent to which benzo(a)pyrene and other polynuclear hydrocarbons are emitted to the atmosphere from some of the more commonly occurring suspect sources is currently being evaluated in a source sampling study by the Public Health Service. A first step in this study was the development of a technique for collecting samples from high temperature combustion and process gas streams in a manner which would assure retention of the hydrocarbon materials of interest. This paper reports the findings of a series of tests conducted (1) to develop suitable methods for cooling the gas samples, (2) to establish temperature requirements for the collected sample during the sampling period, and (3) to evaluate wet versus dry collection techniques.

With a melting temperature of 180°C. and a boiling point near 500°C., benzo(a)pyrene exists in the atmosphere in the solid phase, usually adsorbed on solid particles which can be recovered from the air by filtration.[2] However, in process gas streams the material may be either solid, liquid or gaseous depending on the temperature at the sampling point. Commins and Lawther[2] have demonstrated that benzo(a)pyrene will remain on a filter during sampling when the filter temperature does not exceed 65°F.

These factors dictated the necessity of using a sampling technique which would cool the sample gas stream prior to collecting the condensed and adsorbed material by filtration. Size of the sampling equipment was dictated by requirements of the sampling program which called for 300 to 400 cu. ft. samples in order to assure obtaining comparative data from relatively low concentration sources. To avoid unduly long sampling periods, the equipment was designed to handle flows ranging up to 3.0 scfm.

EXPERIMENTAL PROCEDURE

Samples obtained to date were collected from two combustion sources. These were (1) the stack of an experimental incinerator burning a mixture of newspaper and asphalt felt roofing under controlled combustion conditions, and (2) the exhaust pipe of an automobile operated under controlled conditions on a chassis dynamometer. Simultaneous samples were taken on all but two tests by splitting the sample gas stream into two equal fractions and subjecting each fraction to different collection conditions.

Two methods of cooling the sample gas stream were investigated: (1) by passage through a straight tube metal condenser cooled with circulating ice water prior to collection of the particulate on a filter, hereafter called the dry collection technique, and (2) by passage through a series of water bubblers and condensate traps prior to the final filter collector, hereafter called the wet collection technique. Both sampling trains are shown in Figure 1.

Stainless steel pipette sterilizing cans (2-1/2" diameter x 12" long) were used for the bubblers and condensate traps, all of which were interconnected with 7/16" I.D. stainless steel tubing. These components were followed by a glass fiber filter (MSA type 1106-BH) held in a stainless steel housing and supported by a porous stainless steel plate.

After a very few tests, it became obvious that the dry collection technique, although relatively effective in cooling the gas stream to the desired temperature, had a number of operational limitations, the most serious of which

involved difficulty in recovering that portion of the sample which condensed on or adhered to the condenser tube. Because of this and other drawbacks, work with this technique was discontinued and effort was concentrated on further development of the wet collection technique. A distinct advantage of this latter technique is its greater flexibility in adjusting to wide temperature variations encountered in a field sampling program. Increased cooling capacity can be achieved simply by adding extra bubblers to the existing train.

A series of tests involving both an uncooled filter and wet collection system elements was made to evaluate the suitability of the various combinations of bubblers, condensate traps and filters shown in Figure 2. Samples were collected from the exhaust of a dynamometer-mounted automobile while road load, manifold vacuum and engine rpm were held constant. Each test involved a different combination of operating conditions. Collection train No. 1 was used as the standard collector on all tests, and results from other collection trains are compared to results obtained with this train Temperature of gas flowing through the final condensate trap immersed in the dry ice-acetone bath on train No. 1 was held between 34° and 38°F. In passing from this condensate trap to the filter, the gases warmed sufficiently to produce a filter temperature between 55° and 60°F. which is below the temperature at which Commins and Lawther[2] showed no loss of benzo(a)pyrene. The other collection trains ranged from conditions of no cooling (No. 4) to ice water cooling of one or all bubblers and traps (Nos. 2 and 3).

In processing the collected samples, solid matter was removed from liquid contained in the bubblers and condensate traps by filtering through glass fiber filters (MSA type 1106-BH) which were then allowed to dry at room temperature. Benzene extractions were made of both the water collected fraction and the filter collected fraction, and all containers from the sampling train were rinsed with redistilled benzene. Subsequent evaporation of the benzene was carried out at room temperature by passing a stream of nitrogen over the surface of the samples.

The analytical procedures followed in determining concentration of benzo(a)pyrene in the samples was similar to that described by Sawicki, et al.,[3] in analyzing atmospheric collected particulates for benzo(a)pyrene content. The modifications necessary to adapt this technique to the analysis of source samples will be detailed in a later publication.

RESULTS

Results of tests made to compare the wet and dry collection techniques depicted in Figure 1 are shown in Table I. Although the number of tests made was insufficient to definitely establish the relative collection efficiencies of the two methods, the data does confirm the fact that benzo(a)pyrene can be recovered by either collection technique, if and when the gas stream being tested contains the material of interest. On the first test, the condenser-cooled sample showed 7% more benzo(a)pyrene than the simultaneously collected bubbler-cooled sample, but the duplicate test had 64% less benzo(a)pyrene in

the condenser sample. Time did not permit making additional tests to establish the reason for this variation. The decision to develop the wet collection technique of gas cooling was based on the greater flexibility of the wet technique in adapting to the requirements of a field sampling program and on the operational disadvantages of the dry technique previously mentioned rather than on the above limited data.

Table II gives results of additional tests in which samples were collected in trains as depicted in Figure 2. In these tests, final collection filters were maintained at several different temperatures. Sample gas streams split into two equal portions produced filter temperatures ranging from 132° to 447°F. on the uncooled portions, while the ice water-cooled portions of the gas streams produced filter temperatures ranging from 55° to 95°F. Samples collected on the uncooled filters (No. 4) showed significantly less benzo(a)-pyrene than the corresponding samples collected from the bubbler cooled portions of the gas streams (test Nos. 2 and 3). The filters operated at temperatures above 300°F. showed a maximum of 60% of the benzo(a)pyrene collected on the corresponding low temperature filters which were maintained at 58° and 59°F.

Comparison of results from simultaneously collected bubbler-cooled samples (Test No. 4), in which one filter temperature was above room temperature (95°F.) while the other was below room temperature (57°F.), does not indicate any advantage for the lower collection temperature. Resulting differences in benzo(a)pyrene collected at different temperatures on this test are attributed to experimental error in the sampling and analytical techniques. On tests where dual samples were both collected at approximately the same temperature (61° and 62°F.) the benzo(a)pyrene recoveries showed relatively good consistency (see test No. 6).

Results obtained from the separate analysis of filter-collected material and bubbler-collected material from the same train is shown in Table III and indicate that in most cases only a small portion of the benzo(a)pyrene was collected in the bubblers, the major portion being collected on the filter following the bubbler train.

The bubbler technique of sample collection was found to be satisfactory for continuous sampling for intervals exceeding three hours. Gas volumes in excess of 300 scf were collected and sampling rates up to 2.0 scfm were used. Samples collected at 2.0 scfm from a 1760°F. gas stream were readily cooled to 64°F. at the filter.

The only operational difficulty encountered with the bubbler train involved condensation of moisture on the filter with a resultant increase in pressure drop during sampling. Immersion of the final condensate trap in a dry ice-acetone bath (sampling train No. 1) proved highly effective in removing moisture from the gas stream at this point and served to eliminate this problem.

SUMMARY AND CONCLUSIONS

These tests show that benzo(a)pyrene present in high temperature gas streams can be collected by filtration after cooling the gas to or near ambient temperatures. A series of water bubblers and condensate traps immersed in an ice water bath proved to be a satisfactory technique for this purpose. However, use of a high efficiency filter as the final collector is absolutely necessary since the washing process in the bubblers may remove only a small percentage of the benzo(a)pyrene.

Filter temperatures on the order of 300°F. and above resulted in all or part of the benzo(a)pyrene being lost during sampling. Filter temperatures of 95°F. and below gave generally comparable results. Since the work of Commins and Lawther[2] demonstrated that benzo(a)pyrene suffers little if any loss from the filter during sampling at a filter temperature of 64°F., it is assumed that the collection efficiency of source samples at or near this temperature should be close to 100%.

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TABLE I. RESULTS OF COLLECTING BENZO(a)PYRENE FROM INCINERATOR FLUE GAS BY WET AND DRY SAMPLING TECHNIQUES

Incinerator Operating Conditions		Sampling Train Conditions			Sampling Train Used*	Benzo(a)pyrene Collected (μgm/1000 meters^3 of gas)
Excess combustion air	Flue gas temp. (°F.)	Filter temp. (°F.)	Sampling rate (scfm)	Volume of gas samples (scf)		
70%	1760	63	2.0	91	Wet	5500
		71	2.0	91	Dry	5900
70%	1700	64	2.0	152	Wet	4400
		72	2.0	152	Dry	1600
200%	1085	68	2.0	111	Wet**	0
	1275	71	2.1	116	Dry**	0

* - See Figure 1 for details of wet and dry sampling trains.
** - These were individual rather than simultaneous samples.

TABLE II. EFFECT OF VARYING FILTER TEMPERATURE ON COLLECTION OF BENZO(a)PYRENE FROM AUTO EXHAUST

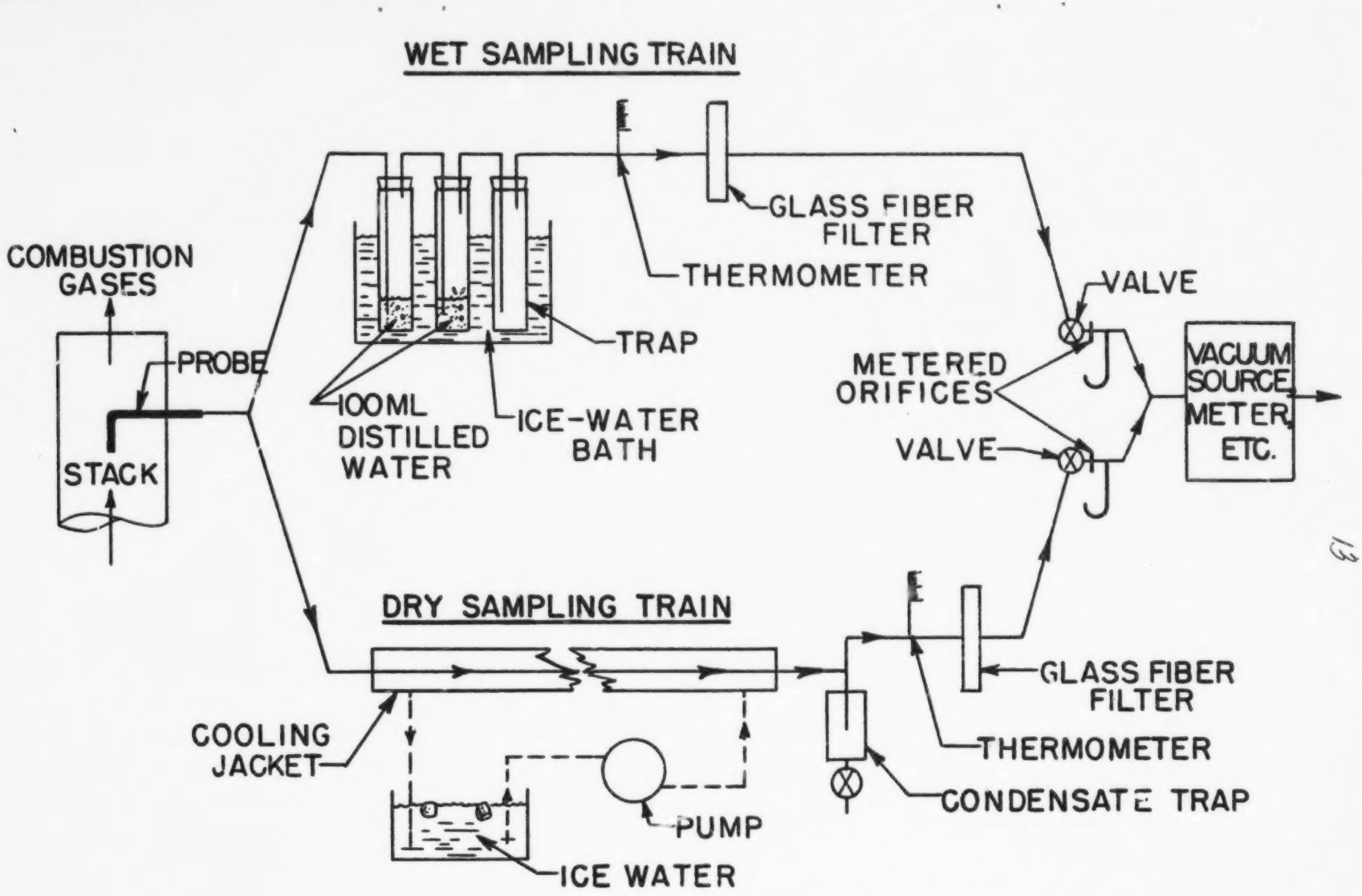
Automobile Test Condition	Gas Temp. at Tailpipe (°F.)	Sampling Train Conditions			Sampling Train Used*	Benzo(a)pyrene Collected (μgm/1000 meters^3 of gas)
		Filter Temp. (°F.)	Sampling Rate (scfm)	Volume of Gas Sampled (scf)		
1	620	58	1.83	329	No. 1	0
		447	1.83	329	No. 4	0
2	560	59	1.19	228	No. 1	3300
		318	1.19	228	No. 4	Trace
3	560	58	1.19	201	No. 1	970
		300	1.19	201	No. 4	580
4	300	57	1.0	202	No. 1	7410
		95	1.0	202	No. 2	8160
5	165	61	1.0	132	No. 1	2600
		62	1.0	132	No. 2	2760

* - See Figure 2 for details of sampling trains.

TABLE III. COMPARISON OF BUBBLER VS. FILTER COLLECTION OF BENZO(a)PYRENE

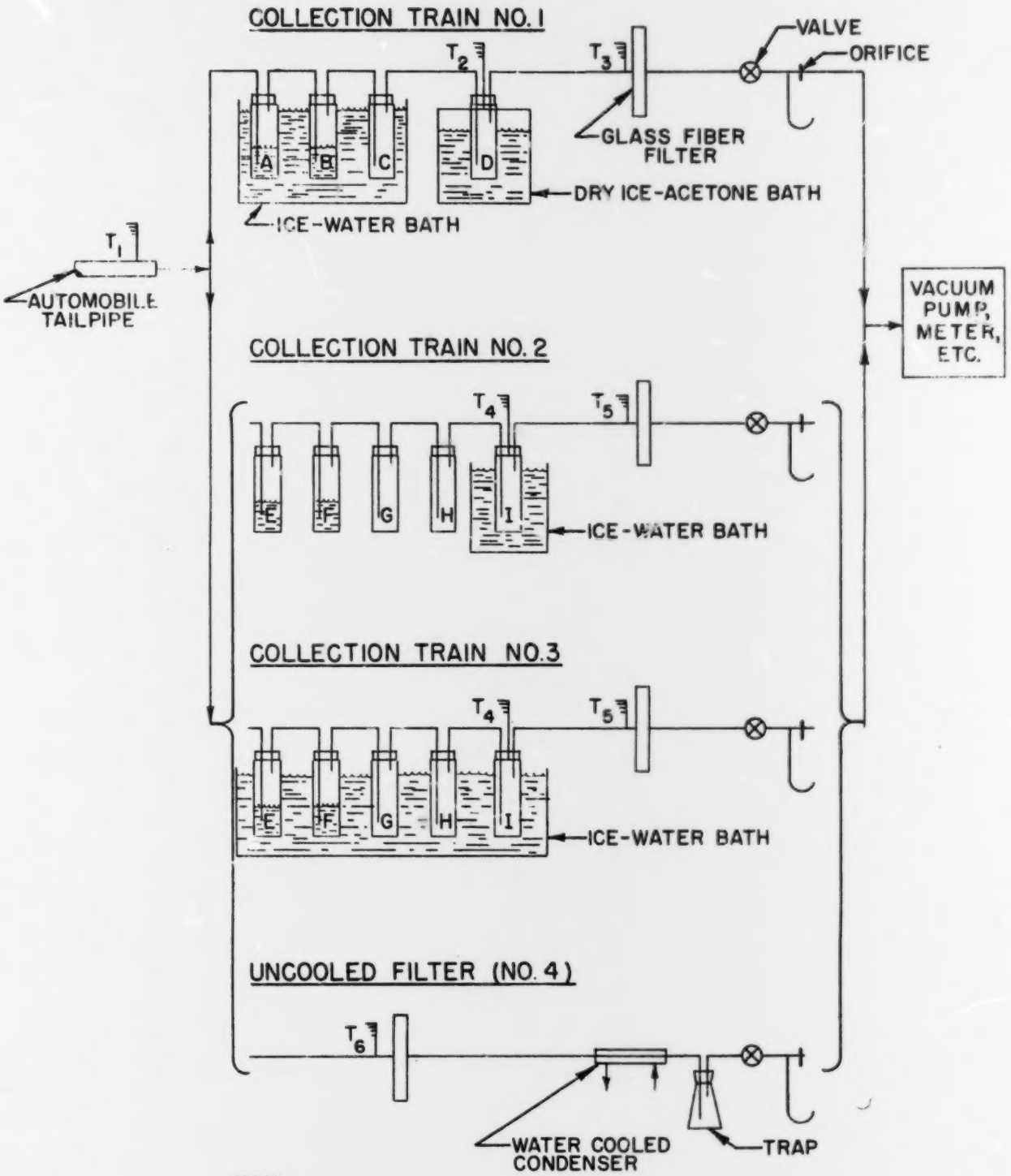
Benzo(a)pyrene Collected (μgm/1000 meters^3 of gas)	Percent Collected		
	On filter	In bubbler water and condensate	In benzene rinse of bubblers
2600	85	15*	—
2760	94	6*	—
3300	61	39*	—
970	65	33	2
7410	84	9	7
8160	91	3	6

* = Includes benzene rinse of bubblers.



SCHEMATIC DIAGRAM OF SPLIT-FLOW SAMPLING APPARATUS USED TO DETERMINE RELATIVE COLLECTION EFFICIENCIES FOR BENZOPYRENE

FIGURE 1



CODE:

A, B, E AND F — METAL BUBBLERS CONTAINING 100ml. DISTILLED WATER

C, D, G, H AND I — METAL TRAPS

T – THERMOMETER

VARIOUS METHODS USED FOR COLLECTING POLYNUCLEAR HYDROCARBON SAMPLES FROM AUTOMOBILE EXHAUST

FIGURE 2